PHYSICAL REVIEW B VOLUME 44, NUMBER 11 15 SEPTEMBER 1991-I

Insulating Cs overlayer on InSb(110)

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(Received 17 May 1991)

Cesium overlayers on room-temperature InSb(110) have been studied with scanning tunneling microscopy and spectroscopy. A two-dimensional (2D) overlayer is observed, consisting of four-atom, Cs(110)-like planar clusters arranged in a $c(2\times6)$ superlattice. Interestingly, current-versus-voltage (I-V) spectra exhibit a band gap of ≈ 0.6 eV, *larger than the substrate band gap* of ≈ 0.15 eV. The I-V spectra are very similar to those observed on the similar 2D overlayer on GaAs(110), suggesting that the measured gap is a property of the 2D Cs film. The possible origins of this insulating behavior are discussed.

Scanning tunneling microscopy and spectroscopy (STM and STS) have been used to investigate the growth of metal overlayers on room temperature III-V semiconductor (110) surfaces.[1-8] The III-V (110) surfaces are appealing for studies of the metal-semiconductor interface since a surface relaxation moves the surface states out of the bulk band gap,[9,10] thereby allowing any metal-induced states within the gap to be more easily observed. Upon adsorption of a metal overlayer different electronic states usually appear within the bulk band edges, so that the band gap observed at the surface is narrower than that of the substrate.[3-8] Metallic characteristics (i.e., states at the Fermi level) are not usually observed until the formation of three-dimensional (3D) multilayer structures.[3,5-8]

In this Rapid Communication we describe the room-temperature properties of Cs overlayers on the narrow-band gap III-V semiconductor InSb(110) (band gap $E_g \approx 0.15$ eV) as determined with STM and STS. A 2D phase of Cs is observed that is composed of four-atom, Cs(110)-like planar clusters arrayed in a $c(2\times6)$ superlattice. Surprisingly, the band gap on this Cs-covered surface is found to be nearly identical to that observed on the similar Cs-covered GaAs(110) surface,[7] $E_g \approx 0.6$ eV, suggesting that this gap is characteristic of the 2D Cs overlayer. To our knowledge, this is the first example of a single layer of adsorbed metal atoms opening up a band gap *larger* than that of the underlying substrate.

The experiments were performed in ultrahigh vacuum on freshly cleaved room-temperature InSb(110) surfaces (n-type, Te doped, 2.5×10^{15} cm^{-3}). The STM has been previously described.[11,12] Prior to mounting the samples in the microscope, Cs was deposited at a rate of $\sim10^{13}$ cm^{-2}s^{-1} using a getter source heated to 625 °C. All STM images shown here were recorded in constant current mode ($I=100$ pA) with a negative sample bias, so that only filled electronic states are observed. The images were recorded with the $+x$ scan direction approximately 45° with respect to the [1$\bar{1}$0] direction, and are displayed uncorrected for thermal drift. Current-versus-voltage (I-V) spectra were obtained by interrupting the STM feedback loop at selected points in the images.[12,13] We define the band gap E_g as the region of an I-V spectrum with zero tunneling conductance, as determined within the noise limit of the data on a more sensitive scale than that shown (Fig. 4). We can measure the width of this region with a precision of approximately 0.1 eV.

The adsorption of Cs on InSb(110) is quite similar to that on GaAs(110), despite the 15% larger lattice constant of InSb. As we previously reported,[7] with increasing coverage on GaAs, insulating 1D zigzag chains are initially observed ($E_g \approx 1.1$ eV), followed by a 2D overlayer ($E_g \approx 0.6$ eV), and finally a metallic 3D bilayer (saturation coverage). On InSb(110), long zigzag chains are also observed at low coverages.[7,14] Similarly, a 2D phase is observed following further Cs exposure, as shown in Fig. 1. An image of a relatively wide area on the surface is displayed in Fig. 1(a), with a Cs coverage estimated to be ≈ 0.5 per InSb(110) unit cell (1.7×10^{14} cm^{-2}). Although the 2D overlayer shown is not perfectly ordered, the highest density well-ordered areas are composed of

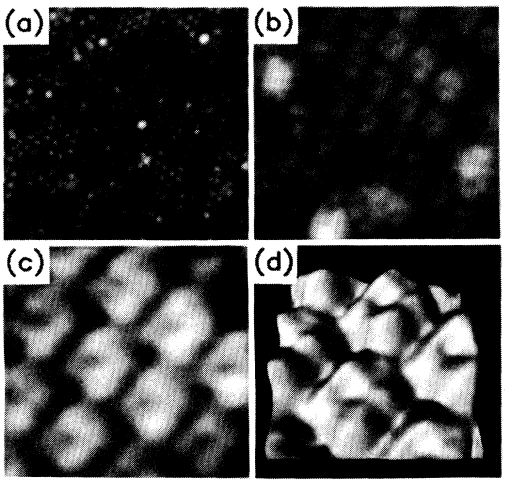

FIG. 1. STM gray-scale topographic images (filled states), with increasing magnification, of a 2D Cs overlayer on room temperature InSb(110): (a) 400×400 Å^2; (b) 100×100 Å^2; (c) 50×50 Å^2; (d) 30×30 Å^2 (rendered as a solid, in perspective). (b)–(d) zoom in on a $c(2\times6)$ ordered area composed of planar Cs clusters. Each cluster appears to have four Cs atoms, topographically ≈ 1 Å high. The Cs coverage, as estimated from the images, is ≈ 0.5 Cs per InSb(110) unit cell (1.7×10^{14} cm^{-2}). Note that the $+x$ scan direction is approximately 45° from the [1$\bar{1}$0] direction, and that the dimensions are uncorrected for thermal drift.

small clusters arranged in a $c(2\times6)$ superlattice. With a slightly larger Cs coverage this $c(2\times6)$ structure completely covers the surface. When the $c(2\times6)$ structure is viewed with successively higher magnification [Figs. 1(b)–1(d)], it becomes apparent that each maximum observed in Fig. 1(a) corresponds to a four-atom planar Cs cluster. Note that no features associated with the substrate atoms are observed in topographs of this structure. A model of the $c(2\times6)$ overlayer is illustrated in Fig. 2, with the assumption that each maximum in the topography of the planar clusters corresponds to the position of an adsorbed Cs atom. The atoms within each cluster appear to be incommensurate with the InSb(110) lattice, with an average nearest-neighbor distance approximately equal to that in bulk Cs, 5.2 Å. Note that the four atoms within each cluster sit in inequivalent adsorption sites, accounting for the different topographic heights observed.

The 2D Cs overlayer on InSb(110) is structurally similar to the one observed on GaAs(110),[7] indicating the importance of Cs-Cs interactions in these overlayers. As on GaAs, each planar cluster on InSb resembles a section of a Cs(110) surface (see Fig. 2), with the structure of each cluster similar to that predicted for the same-size gas-phase cluster.[15] However, interactions with the substrate surface also play a role in determining the structure of the overlayers, as indicated by the well-ordered (but different) superlattices observed on the two surfaces [e.g., on GaAs the clusters have five atoms each and are ordered in a $c(4\times4)$ array[7]]. The distortions within each cluster away from an ideal Cs(110) close-packed structure provide further indication of Cs-substrate interactions; at least in the case of GaAs, where the registry of the Cs clusters with the underlying lattice is more confidently known, the fourfold hollow-like sites between the As atoms seem to be preferred.

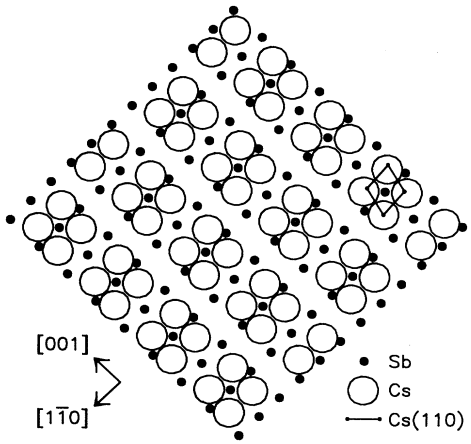

FIG. 2. Schematic model of the $c(2\times6)$ Cs overlayer. The Cs atoms are drawn with 5.2 Å (bulk-like) diameters. Only the Sb lattice is shown for clarity. A segment of a Cs(110) lattice is superimposed over the cluster on the right. The registry of the Cs clusters with the InSb(110) surface is not known, but has been inferred based on similarities with Cs on GaAs(110) (Ref. 7). Note that the Cs density in the ideal $c(2\times6)$ overlayer is $\frac{2}{3}$ Cs per InSb(110) unit cell (2.2×10^{14} cm^{-2}).

When a completed $c(2\times6)$ Cs overlayer on InSb(110) is exposed to further Cs, a second layer begins to grow. As seen in Fig. 3, additional Cs adsorbs on top of the $c(2\times6)$ structure as disordered adatoms and clusters. [The underlying $c(2\times6)$ layer is seen most clearly in the upper-right corner of the image.] Topographic profiles along the surface indicate that the newly adsorbed clusters are a single atomic layer high, i.e., the surface shown is a partly completed disordered bilayer. A range of topographic heights are observed on this surface, which is not surprising given the variety of possible adsorption sites on and between the planar clusters in the first layer. However, there are two dominant topographic heights above the $c(2\times6)$, one corresponding to that expected for a Cs atom adsorbed in a twofold bridge site, and the other for an atom in a fourfold hollow site. Saturation exposure of the surface at room temperature results in a completed (disordered) bilayer, with the $c(2\times6)$ structure no longer visible.

The similar Cs structures observed on InSb and GaAs(110) surfaces share some remarkable electronic properties, as revealed by the I-V characteristics. Typical I-V spectra recorded on the two substrates with the STM tip held over a 1D chain, a 2D overlayer, or a 3D saturation bilayer are compared in Fig. 4. As reproduced in Fig. 4(a), the apparent band gap on a 1D zigzag chain on GaAs(110) is ≈1.1 eV (Ref. 7), reduced from the bulk value of ≈1.5 eV. In contrast, the I-V spectrum on a similar zigzag chain on InSb(110) exhibits a gap approximately equal to that of the substrate, ≈0.15 eV. We believe this may not be a measure of the "chain gap," however, but rather an indication of tunneling into and out of substrate states, for the following reason. As previously described,[7,14] the substrate atoms adjacent to each Cs atom in the chain are clearly visible in the STM topographs of Cs on InSb(110). This shows that electronic states associated with the substrate atoms extend out into the vacuum around each adsorbed Cs atom, and may,

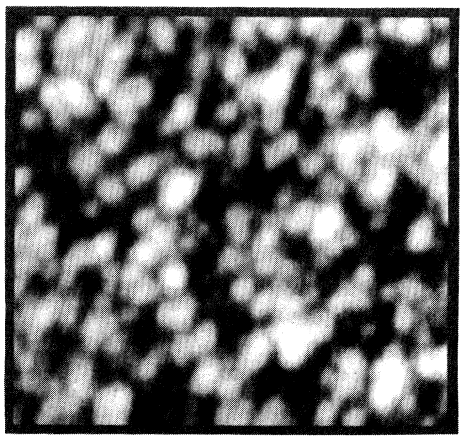

FIG. 3. STM gray-scale topographic image, approximately 400×400 Å^2, of InSb(110) nearly saturated with Cs. The Cs forms a disordered bilayer. A nonlinear gray-scale has been employed in order to make the underlying $c(2\times6)$ layer more visible (see the upper right corner). The gray scale spans approximately 6 Å.

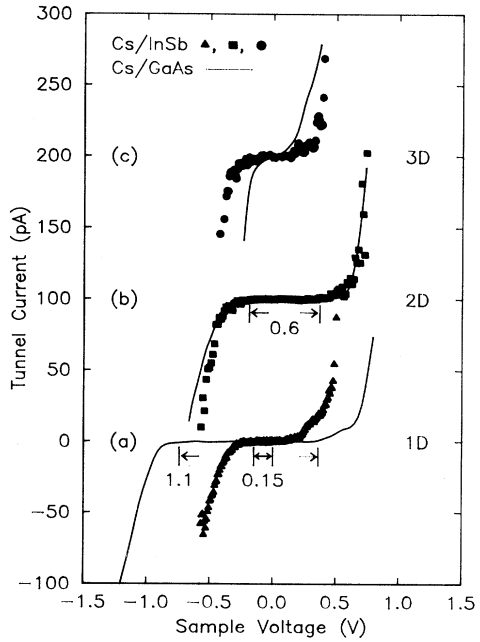

FIG. 4. A comparison of current vs voltage spectra recorded on various Cs structures on InSb(110) (symbols) and GaAs(110) (lines): (a) 1D zigzag chain; (b) 2D overlayer; (c) 3D saturation bilayer. The band gaps indicate the regions of zero conductance (determined on a more sensitive scale). Note that the spectra in (b) and (c) are offset from zero current, and that the GaAs data have been slightly smoothed.

therefore, participate in the tunneling during an I-V measurement (especially when the bias voltage is at a level where there are no states associated with the chain). In consequence, if a larger gap is associated with the chain it will be obscured by tunneling into and out of the adjacent substrate states, and the observed gap will be that of the substrate. Note that this effect was not a problem in determining the band gap on the 1D Cs chain on GaAs(110) because the Cs reduces the gap in that case.

The comparison between the electronic properties of Cs on InSb(110) and GaAs(110) continues in Fig. 4(b) with I-V spectra recorded on 2D overlayers. Surprisingly, the spectra on the two different Cs-covered surfaces *are nearly identical,* with band gaps of ≈ 0.6 eV. This is particularly noteworthy since the gap is *larger* than the InSb band gap. Saturating the InSb surface with additional Cs narrows the observed gap, bringing the surface to a nearly metallic state [$E_g \leq 0.1$ eV; Fig. 4(c)]. While not as clearly metallic as Cs-saturated GaAs(110), examination of the differential conductivity shows that there is nonzero conductivity for all but the smallest voltages ($\leq |0.05|$ V).

To our knowledge, this is the first time a layer of metal atoms has been shown to open up a band gap larger than the bulk band gap of the underlying substrate. One might expect a 2D alkali-metal film to be metallic (in the plane of the film), since the single valence electrons should form a half-filled band of states at the Fermi level. However, if this were the case, the I-V spectrum would not exhibit a band gap. While it is true that the tunneling conductance is usually dominated by substrate electronic states with momentum perpendicular to the surface, tunneling into and out of states with nonzero parallel momentum ($k_\parallel$) can be observed if there are few or no states with $k_\parallel = 0$ within the tunneling energy distribution.[16] The band gap measured with the STM therefore reflects the minimum gap across the whole surface Brillouin zone, not just the gap at the zone center ($k_\parallel = 0$). Since we observe a band gap in the I-V spectrum, we conclude that the 2D Cs overlayer is not metallic, even in the plane of the film. This is truly an insulating overlayer, one in which the InSb substrate states at the interface are not observed to participate in the tunneling.

The remarkable similarity of the I-V spectra for the 2D Cs overlayers on InSb(110) and GaAs(110) suggests that the spectra are characteristic of the Cs overlayer. It is well-known that liquid Cs undergoes a metal-insulator transition at low density due to electron correlation effects, as described by a Mott-Hubbard model,[17] and it has been proposed that the Cs overlayer on GaAs(110) may be an example of a 2D Mott-Hubbard system.[7,18] In this model, the insulating band gap of the overlayer is attributed to the existence of an electron correlation energy U associated with the low Cs density and coordination.[7,18] If the Cs-Cs interactions are strong compared to the Cs-substrate interactions, for which the formation of similar clusters on both substrates provides evidence, then this model would explain the common electronic properties observed on both substrates. Furthermore, it is consistent with the narrowing of the band gap observed upon adsorption of the second Cs layer, since an increase in Cs density and coordination would reduce the electron correlation energy.[17]

While a description of the Cs overlayers in terms of a 2D Mott-Hubbard system is very appealing, there may be an explanation for the observed insulating behavior within a single-particle picture. A recent calculation for Na on GaAs(110) (Ref. 19) found that the alkali-metal valence electron strongly interacts with the empty Ga dangling-bond state, indicating that alkali-substrate interactions may be substantial. If this is the case for Cs, the similar I-V spectra observed on both InSb(110) and GaAs(110) may result from single-particle band structures that are characteristic of similar alkali-substrate interactions. Since GaAs and InSb have similar Phillips ionicities,[20] and Ga and In have nearly the same first ionization energies,[21] it is possible that the two substrates have similar band structures when covered with similar alkali-metal overlayers.

The importance of metal overlayer-substrate interactions in determining the overall surface band structure is illustrated by the insulating (1×1) Sb overlayer on GaAs(110).[1,3] Band structure calculations by Mailhiot, Duke, and Chadi[22] show that, if isolated, the 2D Sb film would be metallic, but that a band gap is opened by the interaction of the hybridized Sb orbitals with the Ga and As dangling bond states (there are two Sb per GaAs unit cell). Furthermore, although the measured electronic structure of a (1×1) Sb overlayer on InSb(110) has yet to be reported, the calculated states for such a surface are

very similar to those on GaAs(110).[22] There is an important difference, however, between these Sb overlayers and the Cs overlayers we observe (which appear to interact primarily with the surface Ga or In atoms). A (1×1) Sb overlayer on a III-V (110) surface has an even number of valence electrons per surface unit cell, and is therefore expected to be nonmetallic. In contrast, a Cs overlayer bonded only to surface Ga or In atoms has an odd number of valence electrons, and one therefore expects a half-filled, metallic band of states. An accurate calculation of the band structures for the actual 2D Cs overlayers on GaAs(110) and InSb(110) is required to determine if single-particle effects explain the observed band gaps. It is possible that even when Cs-substrate interactions are included, correlation effects will be necessary to account for the insulating character of these surfaces.

If the alkali-metal overlayers truly are 2D Mott-Hubbard systems, they will have interesting magnetic properties which should be observable in the laboratory.[23,24] For example, a 2D Mott-Hubbard system will exhibit antiferromagnetic ordering at the Néel temperature, $k_B T_N \simeq 2t^2/U$, where U is the intrasite Coulomb interaction energy between two electrons on the same site (the electron correlation energy, ≈ 0.6 eV in this case), and t is the interaction energy between electrons on neighboring sites.[23] The interaction energy t is approximately equal to the dispersion of the donor state (or acceptor state) energy level [the level associated with the presence of one (or two) electrons on a single site],[24] and therefore should be measurable via angle-resolved photoemission spectroscopy. (Assuming $T_N < 300$ K, the dispersion should be very small, < 0.1 eV.) If the Néel temperature is experimentally accessible, it should be possible to observe the antiferromagnetic transition with low-energy electron diffraction from the alkali-metal overlayer, since the expected magnetic ordering will change the periodicity of the electron scattering.

In summary, we have studied the room-temperature adsorption of Cs on the (110) surface of the narrow-band-gap semiconductor InSb with scanning tunneling microscopy and spectroscopy. Insulating 1D zigzag chains are observed at low coverages, as previously reported.[7] With increasing coverage a 2D overlayer is observed, composed of four-atom, Cs(110)-like planar clusters ordered in a $c(2\times6)$ superlattice. Additional Cs exposure leads to the growth of a disordered second layer on top of the $c(2\times6)$ structure, and a transition to near metallic conductance ($E_g < 0.1$ eV). Remarkably, the 2D $c(2\times6)$ overlayer is found to have a band gap of ≈ 0.6 eV, which is *larger than that of the underlying InSb substrate,* and nearly identical to that observed for the similar 2D overlayer on GaAs(110). The similarities between the adsorption of Cs on InSb and GaAs suggest that the observed electronic properties are characteristic of a 2D Cs overlayer, which may be an example of a 2D Mott-Hubbard insulator. Alternatively, the band gap may result from single-particle band structure effects associated with characteristic Cs-substrate interactions. Clearly, further experimental and theoretical work is needed to elucidate the physical mechanisms underlying this interesting result.

We are grateful to Dr. M. D. Stiles and Dr. D. T. Pierce for many useful discussions. This work was supported in part by the Office of Naval Research.

[1]R. M. Feenstra and P. Martensson, Phys. Rev. Lett. **61**, 447 (1988); P. Martensson and R. M. Feenstra, Phys. Rev. B **39**, 7744 (1989).

[2]C. K. Shih, E. Kaxiras, R. M. Feenstra, and K. C. Pandey, Phys. Rev. B **40**, 10044 (1989).

[3]C. K. Shih, R. M. Feenstra, and P. Martensson, J. Vac. Sci. Technol. A **8**, 3379 (1990).

[4]A. B. McLean, R. M. Feenstra, A. Taleb-Ibrahimi, and R. Ludeke, Phys. Rev. B **39**, 12925 (1989).

[5]R. M. Feenstra, Phys. Rev. Lett. **63**, 1412 (1989); J. Vac. Sci. Technol. B **7**, 925 (1989).

[6]P. N. First, Joseph A. Stroscio, R. A. Dragoset, D. T. Pierce, and R. J. Celotta, Phys. Rev. Lett. **63**, 1416 (1989).

[7]L. J. Whitman, Joseph A. Stroscio, R. A. Dragoset, and R. J. Celotta, Phys. Rev. Lett. **66**, 1338 (1991).

[8]M. Prietsch, A. Samsavar, and R. Ludeke, Phys. Rev. B **43**, 11850 (1991).

[9]X. Zhu, S. B. Zhang, S. G. Louie, and M. L. Cohen, Phys. Rev. Lett. **63**, 2112 (1989), and references therein.

[10]H. Carstensen, R. Claessen, R. Manzke, and M. Skibowski, Phys. Rev. B **41**, 9880 (1990).

[11]R. D. Cutkosky, Rev. Sci. Instrum. **61**, 960 (1990).

[12]L. J. Whitman, Joseph A. Stroscio, R. A. Dragoset, and R. J. Celotta, Phys. Rev. B **42**, 7288 (1990).

[13]R. M. Feenstra and Joseph A. Stroscio, J. Vac. Sci. Technol. B **5**, 923 (1987).

[14]L. J. Whitman, Joseph A. Stroscio, R. A. Dragoset, and R. J. Celotta, J. Vac. Sci. Technol. B **9**, 770 (1991).

[15]V. Bonacic-Koutecky, P. Fantucci, I. Boustani, and J. Koutecky, in *Studies in Physical and Theoretical Chemistry* (Elsevier, Amsterdam, 1989), Vol. 62, p. 429.

[16]Joseph A. Stroscio, R. M. Feenstra, and A. P. Fein, Phys. Rev. Lett. **57**, 2579 (1986); R. M. Feenstra, Joseph A. Stroscio, and A. P. Fein, Surf. Sci. **181**, 295 (1987).

[17]D. E. Logan and P. P. Edwards, in *The Metallic and Nonmetallic States of Matter,* edited by P. P. Edwards and C. N. R. Rao (Taylor & Francis, London, 1985), pp. 78–81; W. Freyland and F. Hensel, *ibid.* pp. 93–121, and references therein.

[18]N. J. Dinardo, T. M. Wong, and E. W. Plummer, Phys. Rev. Lett. **65**, 2177 (1990).

[19]J. Hebenstreit, M. Heinemann, and M. Scheffler, Phys. Rev. Lett. **67**, 1031 (1991).

[20]J. C. Phillips, Rev. Mod. Phys. **42**, 317 (1970).

[21]L. Pauling, *The Nature of the Chemical Bond,* 3rd ed. (Cornell University, Ithaca, 1960), p. 57.

[22]C. Mailhiot, C. B. Duke, and D. J. Chadi, Phys. Rev. Lett. **53**, 2114 (1984); Phys. Rev. B **31**, 2213 (1985).

[23]S. Doniach, Advan. Phys. **18**, 819 (1969).

[24]C. B. Duke and W. K. Ford, Surf. Sci. **111**, L685 (1981).